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RESEARCH ON RARE-EARTH METALS AND COMPOUNDS AND DEVELOPMENT OF APPLICATIONS BASED ON THEIR MAGNETIC PROPERTIES

Semi-Annual Technical Report
(2 November 1970 - 1 May 1971)

by

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13. ABSTRACT

This report describes the technical accomplishments of the first six-month phase of a research program on the magnetic and magnetoelastic properties of the rare-earth elements and alloys and compounds rich in the rare earths. A primary goal of this program is the development of highly efficient high-frequency ultrasonic transducers utilizing the extremely high magnetostriction found in most rare-earth materials. Three major projects have been carried out during the period covered by this report. First, ultrasonic transducers in the form of thin polycrystalline films deposited on nonmagnetic substrates have been constructed using pure rare earths. These transducers have been used successfully to produce intense ultrasonic waves in the microwave frequency range. Second, in order to better understand the magnetoelastic coupling which is responsible for the large magnetostriction of the rare earths, studies have been made on the attenuation and velocity of 20 MHz ultrasonic waves at various temperatures in single-crystal rare-earth material as a function of applied magnetic field. The results show an extremely strong magnetoelastic interaction in the case of terbium crystals, and these results lead to the conclusion that dynamic magnetostriction in the rare earths can be used for ultrasonic generation at high efficiency. The results also indicate the possibility of the development of efficient ultrasonic switches and modulators for high-frequency operation. Finally, an effort has been made to construct apparatus for

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the preparation of single-crystal specimens of rare-earth materials for use in this program. The apparatus has been constructed, but certain refinements are still in progress, and it is not yet possible to grow single crystals reliably with this apparatus.

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Abstract

This report describes the technical accomplishments of the first six-month phase of a research program on the magnetic and magnetoelastic properties of the rare-earth elements and alloys and compounds rich in the rare earths. A primary goal of this program is the development of highly efficient high-frequency ultrasonic transducers utilizing the extremely high magnetostriction found in most rare-earth materials. Three major projects have been carried out during the period covered by this report. First, ultrasonic transducers in the form of thin polycrystalline films deposited on nonmagnetic substrates have been constructed using pure rare earths. These transducers have been used successfully to produce intense ultrasonic waves in the microwave frequency range. Second, in order to better understand the magnetoelastic coupling which is responsible for the large magnetostriction of the rare earths, studies have been made on the attenuation and velocity of 20 MHz ultrasonic waves at various temperatures in single-crystal rare-earth material as a function of applied magnetic field. The results show an extremely strong magnetoelastic interaction in the case of terbium crystals, and these results lead to the conclusion that dynamic magnetostriction in the rare earths can be used for ultrasonic generation at high

efficiency. The results also indicate the possibility of the development of efficient ultrasonic switches and modulators for high-frequency operation. Finally, an effort has been made to construct apparatus for the preparation of single-crystal specimens of rare-earth materials for use in this program. The apparatus has been constructed, but certain refinements are still in progress, and it is not yet possible to grow single crystals reliably with this apparatus.

LIST OF FIGURES

I. INTRODUCTION

This report describes the technical achievements attained during the first six-month period of a research program entitled "Research on Rare-Earth Metals and Compounds and Development of Applications Based on Their Magnetic Properties." This program is sponsored by the Advanced Research Projects Agency (ARPA Order 1685) and administered by the U. S. Army Missile Command (Contract DAAH01-71-C-0259). The principal emphasis in this research program is directed toward the ultimate exploitation of the extremely large magnetostriction characteristic of many of the rare-earth elements for the generation of ultrasonic waves at very high intensity and at very high frequency. The very intense, high-frequency, elastic waves which could be produced as the result of the successful development of rare-earth transducers would find many useful technological applications in such areas as non-destructive testing of solids, investigation of the anelastic properties of solids, microwave-frequency communications and signal processing systems, and the rapidly growing field of acoustical holography.

Although the complete research program will include a rather broad range of investigations, the work carried out during the first six-month period has been concentrated on three major areas.

Each of these areas of initial effort is of fundamental importance to the entire program, but they are particularly important for the initial phase of the program because they all require the development of experimental techniques which are essential to the remaining areas of research to be pursued during the second six-month period of this program.

The first project to be described in this report is the one most directly connected with the primary goal of the program. This project is an investigation of high-frequency ultrasonic generation by means of magnetoelastic interactions in polycrystalline films of pure rare-earth metals. Although it is unlikely that the full potential capability of the rare earths as ultrasonic transducers can be achieved through the use of polycrystalline films, such films are readily prepared from commercially available polycrystalline material of high purity, and they have, in fact, yielded very encouraging results during the initial phase of investigation. In particular, the rare-earth films which have already been investigated are much more efficient in the microwave-frequency range than single-crystal quartz, the transducer material most widely used at present in this frequency range.

The second project to be undertaken during the initial phase of this research program is concerned with the propagation of ultrasonic waves in the 20-MHz frequency range through single-

crystal specimens of pure rare-earth metals. Because the magnetostrictive generation of ultrasonic waves depends on the reciprocal coupling between spin waves and elastic waves, the nature of this coupling, which must be understood from a fundamental point of view in order to permit the intelligent design of transducers, may be deduced from studies of the attenuation and velocity dispersion of conventionally produced ultrasonic waves travelling through rare-earth crystals. The most straightforward information to be obtained from such an investigation is the quantitative values of the normal elastic constants, which have not been reported previously for most of the rare earths. From the point of view of the overall goals of this research project, however, measurements of the field dependence and temperature dependence of ultrasonic attenuation provide direct information concerning the fundamental magnetoelastic interaction. In the case of terbium, the material upon which the work has been concentrated initially, the dependence of the ultrasonic attenuation on magnetic-field strength is so strong that an unexpected potential application of terbium as an ultrasonic attenuator, modulator, or switch has emerged.

The third project described in this report is concerned with the preparation of single-crystal rare-earth materials, particularly alloys and intermetallic compounds. Since it is possible

to produce a wide range of variation of most of the magnetic properties of materials containing rare earths by means of relatively small variations in composition, it will be necessary to investigate a large number of different materials in order to determine those most suitable for use as magnetostrictive transducers. A floating-zone, induction-heated, crystal-growing system has been constructed to permit the growth of single-crystal alloys of arbitrary composition. This technique has been used successfully for this purpose, and the present effort has been directed toward the construction of a system capable of simple and reliable operation. The system is nearing completion, and it has been used in preliminary tests with pure rare-earth specimens with encouraging results.

These three projects are described in detail in the following sections of this report, and their extension into the second six-month phase of the program is discussed, together with their relation to other areas of research which will commence during the coming months.

II. DESCRIPTION OF RESEARCH

1. Thin-Film Ultrasonic Transducers

The generation of ultrasonic waves at microwave frequency by means of magnetoelastic interactions in thin polycrystalline films of magnetic materials has been investigated thoroughly for a number of different materials, although by far the most complete study of this phenomenon is that of Seavey[1], who investigated ultrasonic generation in permalloy films. The first report of ultrasonic generation in rare-earth films was that of Maley, Donoho, and Blackstead[2], who observed strong ultrasonic generation in films of gadolinium, dysprosium, holmium, and erbium. The research described in this report has been directed toward extension of the results of Maley *et al*. as a preliminary step in a program which will include ultrasonic generation in transducers made of rare-earth single crystals and both polycrystalline and single-crystal transducers made of rare-earth alloys and compounds.

In a number of ways the use of polycrystalline films as ultrasonic transducers is highly desirable, since they can be readily deposited on materials through which it is desired to propagate elastic waves. The film thickness may be adjusted to provide elastic-wave resonance at a given frequency in order to enhance the ultrasonic generation. Finally, the large magneto-

crystalline anisotropy characteristic of the rare earths is averaged essentially to zero in a polycrystalline specimen, so that extremely careful alignment of both the dc magnetic field and the rf magnetic field which excites the waves is not required.

On the other hand, a principal disadvantage to the use of polycrystalline transducers, at least in the case of the pure rare earths, is the fact that the averaging of the anisotropy is accompanied by a similar averaging effect in the case of the magnetostriction, which is closely related to the magnetocrystalline anisotropy. It would not be expected, therefore, that the full potential of the rare earths for efficient ultrasonic generation could ever be realized in the case of polycrystalline samples, although the efficiency should still be substantially higher than that of most other high-frequency transducer materials. In the work reported here, it has, in fact, been found that polycrystalline rare-earth transducers do appear to be much more efficient for ultrasonic generation in the microwave frequency range than any of the piezoelectric or iron-group magnetostrictive materials commonly employed as ultrasonic transducers. As a result, the investigation of the characteristics of polycrystalline transducers has been more extensive than originally planned, so that the investigation of single-crystal transducers has been deferred until the second six-month phase of this research program.

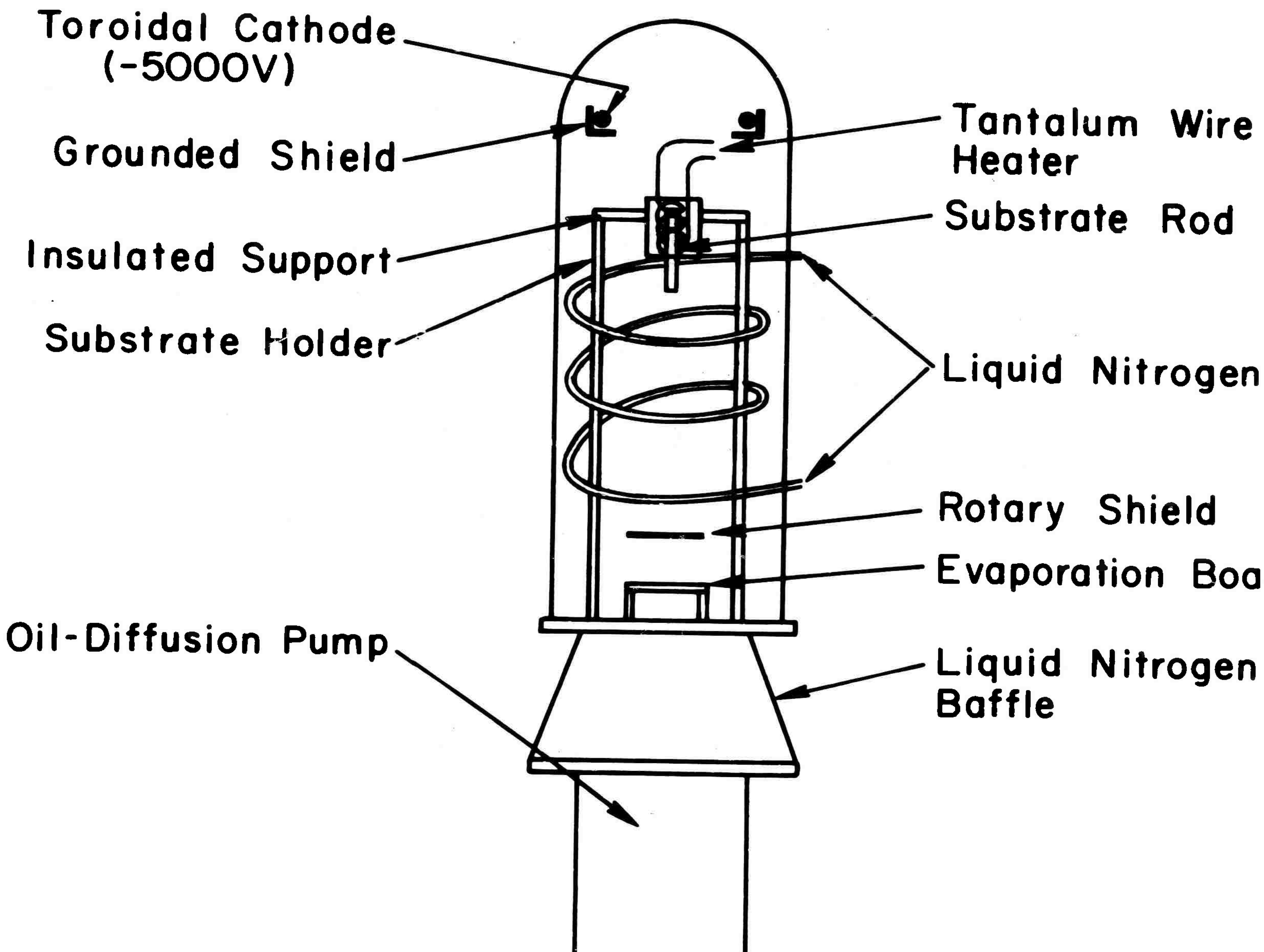
The following description of the results obtained during the period covered by this report is divided into three parts: (a) sample preparation, (b) experimental techniques, and (c) results and interpretation. A discussion of the way in which this work will be carried into the next phase of the program is contained in section III of the report.

(a) Sample Preparation

The experimental work on ultrasonic generation is done in a manner quite similar to the usual ultrasonic experiment utilized for the measurement of elastic constants. A transducer is bonded to one end of a nonmagnetic substrate, the ultrasonic waves are generated magnetically within the transducer, and they propagate back and forth through the substrate material, giving rise to a set of pulse echoes which are detected by the reciprocal conversion of elastic-wave energy into magnetic energy. In the present case, the transducer is in the form of a film of thickness in the range of 1-2 microns deposited onto the substrate by means of vacuum evaporation. Because the rare earths are all highly reactive chemically, special precautions must be taken in the deposition of the film to insure that it remain relatively pure during and after the deposition.

The vacuum-deposition apparatus is shown in Figure 1. A conventional high-speed oil-diffusion vacuum system is employed for the sample preparation, with the substrate and evaporant located inside a pyrex bell jar. The rare-earth material to be evaporated is placed in a tungsten boat, and it is initially outgassed at a temperature just below the melting point of the rare earth. The substrate on which the film is to be deposited is maintained at a temperature of 350° C before and during the deposition of the film in order to provide outgassing and to increase the mobility of the atoms in the film during deposition. This substrate heating provides much cleaner and more uniform films than can be obtained with a substrate at ambient temperature. In addition to the conventional liquid-nitrogen trap at the entrance to the diffusion pump, a "Meissner" trap at liquid-nitrogen temperature is placed within the bell jar primarily to trap water vapor, which interferes greatly with the formation of a uniform film. Before deposition of the film, the substrate is cleaned by means of ion bombardment in a glow discharge. The film is deposited immediately after this procedure, and it is immediately coated with a protective film of silicon monoxide. During the deposition, the evaporating rare earth coats the inside of the bell jar, providing a large surface of pure rare-earth metal to trap the remaining oxygen and other contaminants inside the bell jar. The

Figure 1. Schematic diagram of system for deposition of thin films of rare-earth materials by vacuum evaporation.


Toroidal Cathode
(-5000V)
Grounded Shield
Insulated Support
Substrate Holder
Oil-Diffusion Pump
Tantalum Wire
Heater
Substrate Rod
Liquid Nitrogen
Rotary Shield
Evaporation Boat
Liquid Nitrogen
Baffle

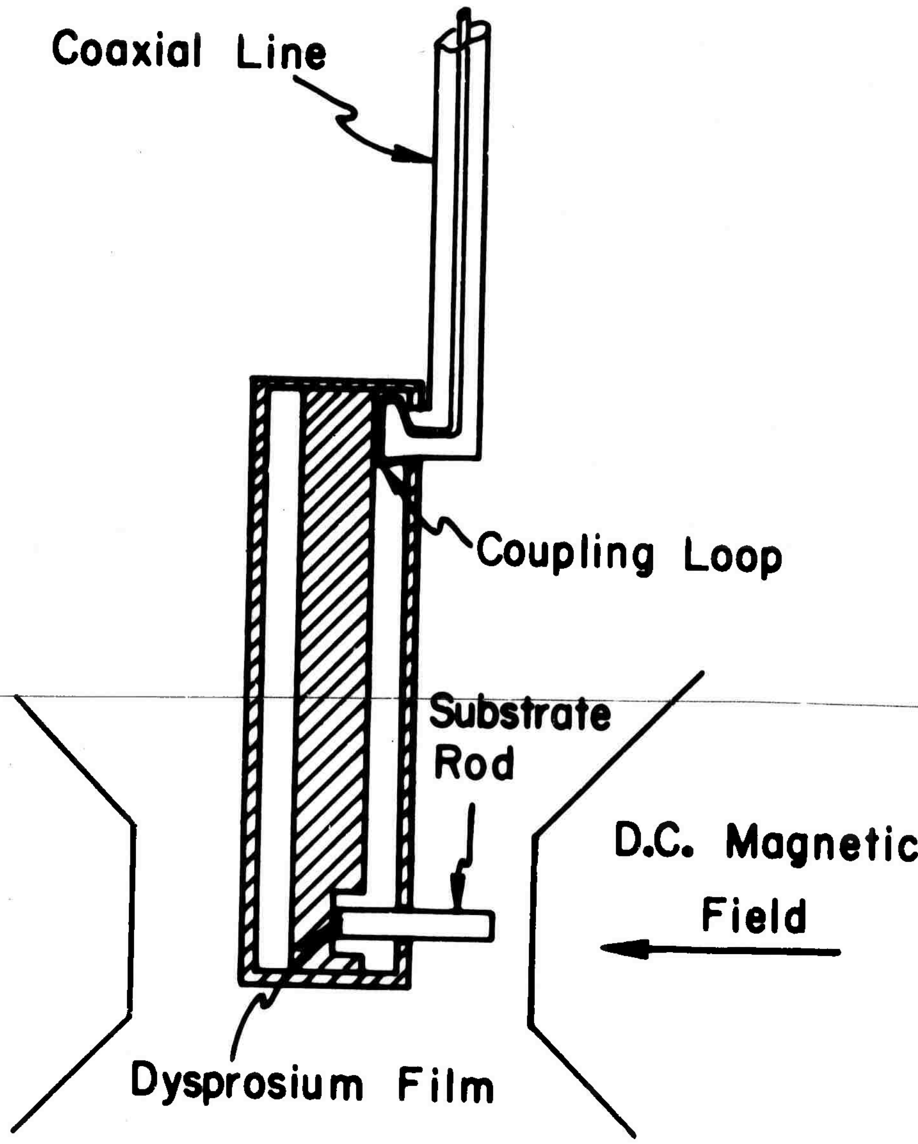
film thickness is monitored by means of a quartz-crystal microbalance. By means of these techniques, films of known thickness and reproducible characteristics may be readily produced on a variety of substrate materials.

Films of gadolinium, dysprosium, holmium, and erbium have been successfully deposited on substrates of quartz, corundum, and magnesium oxide (all in single-crystal form), and all have yielded strong ultrasonic generation at frequencies from 1.0 GHz up to 9.3 GHz, as described below.

(b) Experimental Techniques

The polycrystalline films deposited on the end of single-crystal substrate rods were investigated by inserting them into a microwave resonant cavity in such a manner that the rf magnetic field within the cavity was parallel to the surface of the film. A typical cavity employed in the 1.0-GHz frequency range is shown in Figure 2; at higher frequencies, a rectangular cavity was used. The cavity was placed inside a cryostat within which the temperature of the sample film could be maintained at any desired value between 300 K and 1.5 K. The cryostat was located between the pole faces of an electromagnet capable of producing a field of 20 kG. The magnet could be rotated so that the field was directed parallel or perpendicular to the surface of the film (or at any oblique

Figure 2. Cavity employed for excitation of ultrasonic waves by means of magnetostriction in rare-earth thin films at 1,000 MHz.


Coaxial Line
Coupling Loop
Substrate Rod
D.C. Magnetic Field
Dysprosium Film

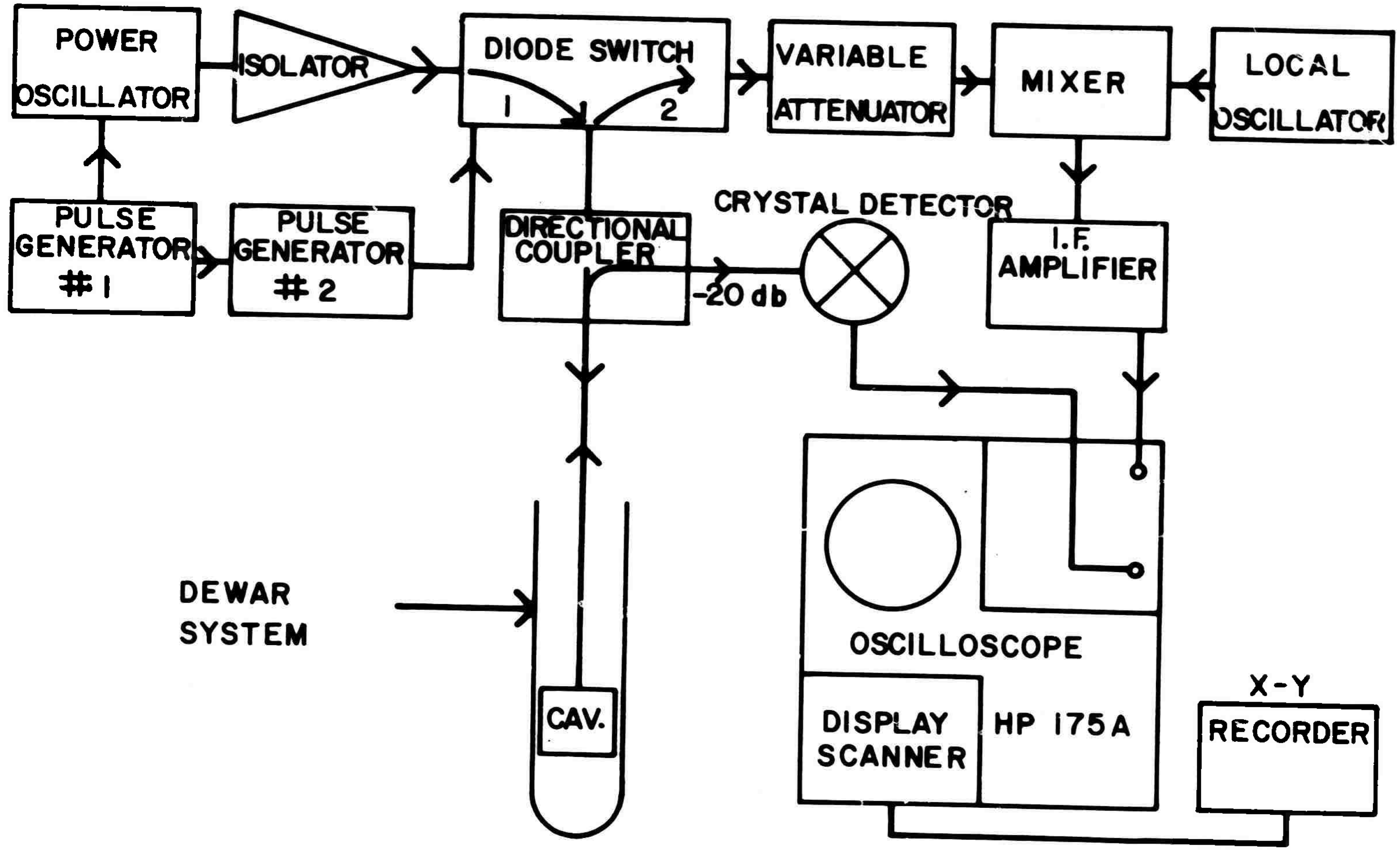
angle, if desired). The temperature of the sample was monitored by means of a thermocouple embedded in the cavity wall.

A schematic block diagram of the experimental apparatus is shown in Figure 3, for the case of operation at a frequency of approximately 1.0 GHz. The tunable power oscillator delivered a pulse of peak power 10-20 W, and the diode switch served as a duplexer to switch the cavity alternately between the transmitter and the receiver. A standard superheterodyne receiver was employed. After excitation of the ultrasonic waves by a pulse from the oscillator, a series of pulse echoes could be observed on the oscilloscope, and the amplitude of any desired echo could be accurately monitored by means of a synchronous sampling "boxcar" integrator. The dependence of the ultrasonic amplitude, proportional to the amplitude of any of the echoes displayed on the screen of the oscilloscope, could thus be determined as a function of the strength or direction of the magnetic field or as a function of the sample temperature. Examples of the results obtained are presented in the following section of this report.

(c) Results and Interpretation

The results which have been obtained up to the present time in this investigation have been quite interesting and encouraging, but it should be emphasized that the results reported here are

Figure 3. Schematic diagram of experimental apparatus for the generation and detection of 1,000-MHz ultrasonic waves by means of magnetostriction.


POWER OSCILLATOR
ISOLATOR
DIODE SWITCH
1
2
VARIABLE ATTENUATOR
MIXER
LOCAL OSCILLATOR
PULSE GENERATOR #1
PULSE GENERATOR #2
DIRECTIONAL COUPLER
CRYSTAL DETECTOR
-20 db
I.F. AMPLIFIER
DEWAR SYSTEM
CAV.
OSCILLOSCOPE
DISPLAY SCANNER
HP 175A
X-Y RECORDER

preliminary in nature and that their interpretation cannot be considered complete. Most of the present uncertainty in the interpretation of the results comes, however, from the polycrystalline nature of the sample films, and it is certain that work which is just beginning on single-crystal transducers will soon permit a more complete understanding of the results obtained with polycrystalline films.

A polycrystalline film with a truly random array of microscopic crystallites would normally be expected to exhibit rather isotropic magnetic, magnetoelastic, and elastic properties, each representing a suitable average of the corresponding single-crystal properties. For materials such as pure dysprosium, holmium, or terbium, however, the actual calculation of the appropriate polycrystalline average for the magnetic or magnetoelastic properties is quite difficult because of the extremely large magnetocrystalline anisotropy. Thus, without rather detailed measurements, utilizing single-crystal specimens, of the same dynamic magnetoelastic properties as those of interest for the polycrystalline thin films, it may be impossible to relate the observed polycrystalline properties to the presently understood single-crystal properties. For example, dysprosium forms a hexagonal close-packed (hcp) crystal lattice in which the anisotropy forces the spontaneous magnetization to lie along the a-direction

in the basal plane. The frequency at which magnetic resonance can occur, accompanied by a resonant dynamic elastic strain due to the magnetoelastic coupling, depends strongly on the magnitude and direction of the applied magnetic field. In fact, only for a very narrow range of field strength and direction can a resonance be excited at microwave frequency. Yet, in a polycrystalline film placed in a uniform field, each crystallite experiences a different direction and, possibly, a different strength, of the local field. Thus, only a small fraction of the crystallites will normally exhibit resonance and the consequent large ultrasonic generation if the sample is truly random in crystallite orientation. There is, however, evidence that the crystallite orientation is not random and that anisotropy forces during the high-temperature film deposition provide some preferential alignment of the crystallites. Thus, the observed ultrasonic generation is stronger than would be expected for a completely random sample. It has not, however, been possible to calculate the degree of non-random alignment or to determine ways of augmenting the alignment. Thus, the present understanding of the results discussed below is based on a rather limited knowledge of the film characteristics, and further experimental and theoretical work is needed in order to advance this understanding.

The most complete work to date has been carried out on films of relatively pure dysprosium deposited on single-crystal quartz substrates with the film normal to the crystallographic x-axis. This choice of the substrate and its orientation was based on the fact that ultrasonic waves can be excited piezoelectrically in the quartz without a transducer, so that the suitability of the substrate for the propagation of ultrasonic waves at microwave frequency may be easily determined before film deposition. Furthermore, for this orientation of the substrate, the velocities of the three independent ultrasonic modes are all different, thus permitting easy identification of the particular ultrasonic mode generated by the rare-earth film. To a less complete extent, results have also been obtained with films of gadolinium, holmium, and erbium, and substrates of aluminum oxide and magnesium oxide have been employed. Although the results obtained with gadolinium are at present the easiest to interpret, the relatively low magnetostriction of gadolinium makes this material relatively less interesting than the other magnetic rare earths. The results obtained with each material investigated to date are presented below.

<u>Dysprosium</u>: The magnetic-field dependence of the ultrasonic generation in dysprosium is strikingly dependent upon the direction of the field with respect to the plane of the film, as indicated in Figures 4 and 5. In Figure 4, which shows the results obtained

Figure 4. Dependence of ultrasonic generation in dysprosium thin films on applied magnetic field strength and temperature. The frequency is 1,000 MHz, and the magnetic field is perpendicular to the plane of the film.

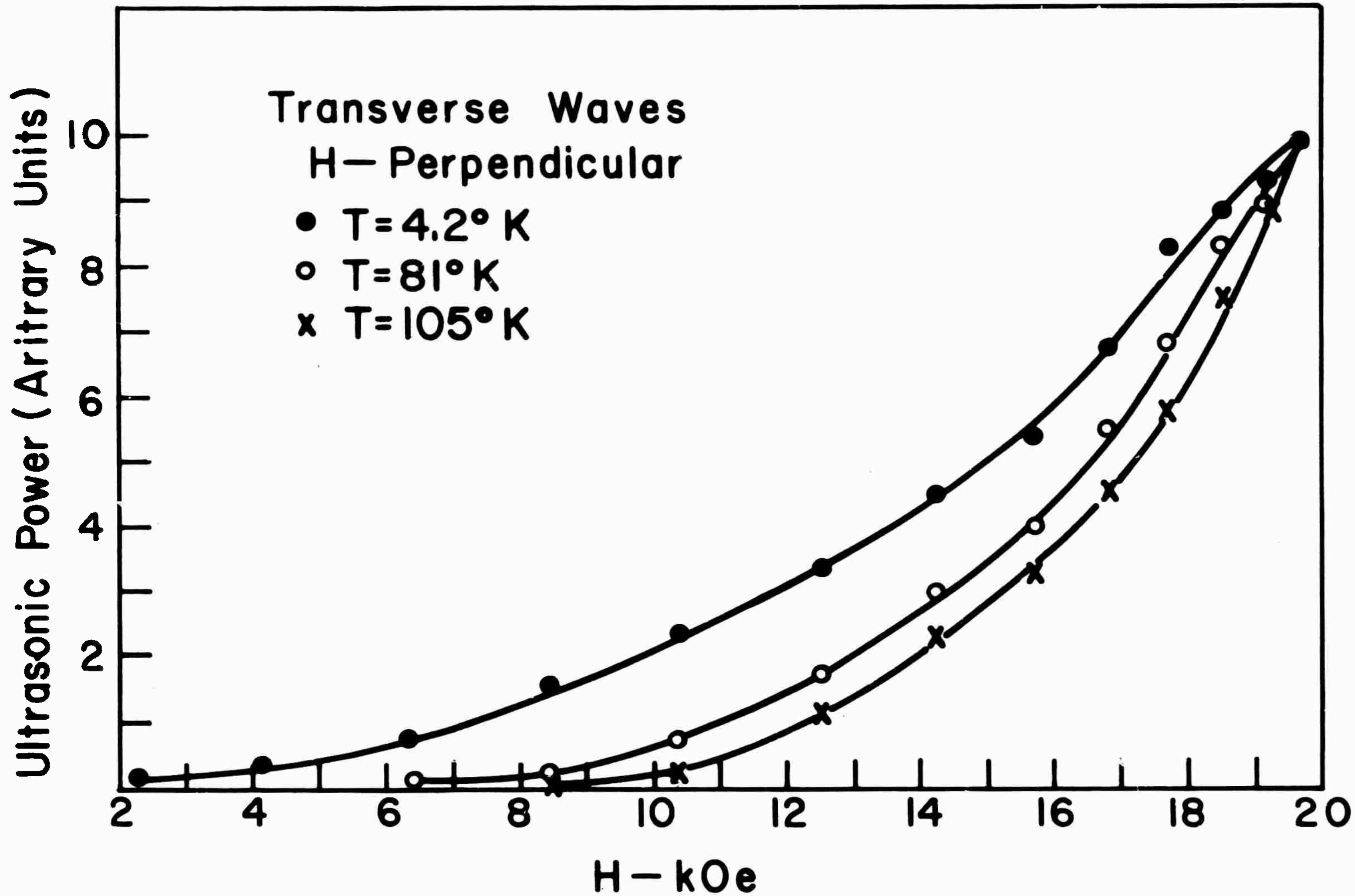
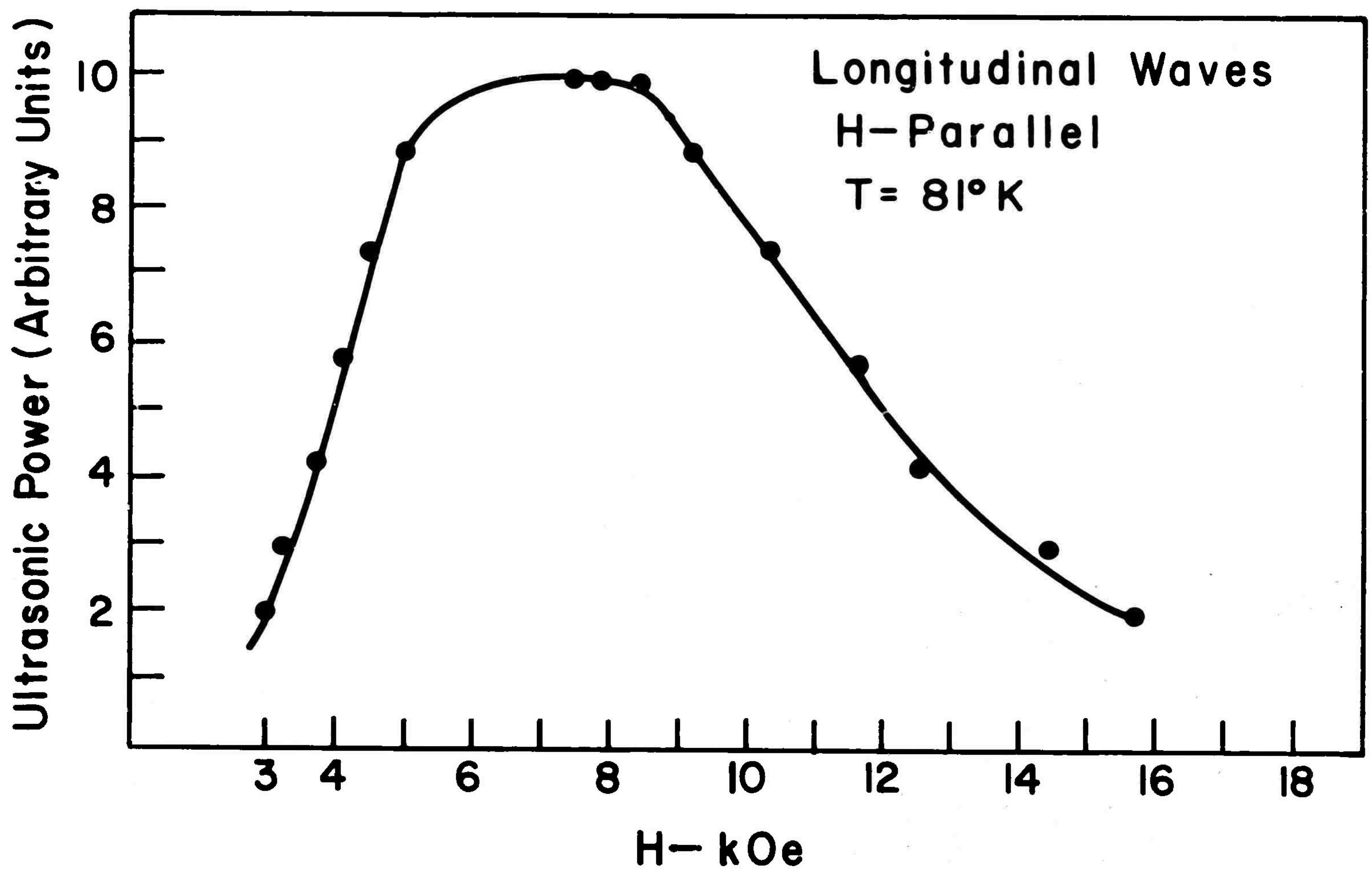

Transverse Waves
H — Perpendicular
● T = 4.2° K
○ T = 81° K
x T = 105° K
Ultrasonic Power (Aritrary Units)
H — kOe
2
4
6
8
10
12
14
16
18
20

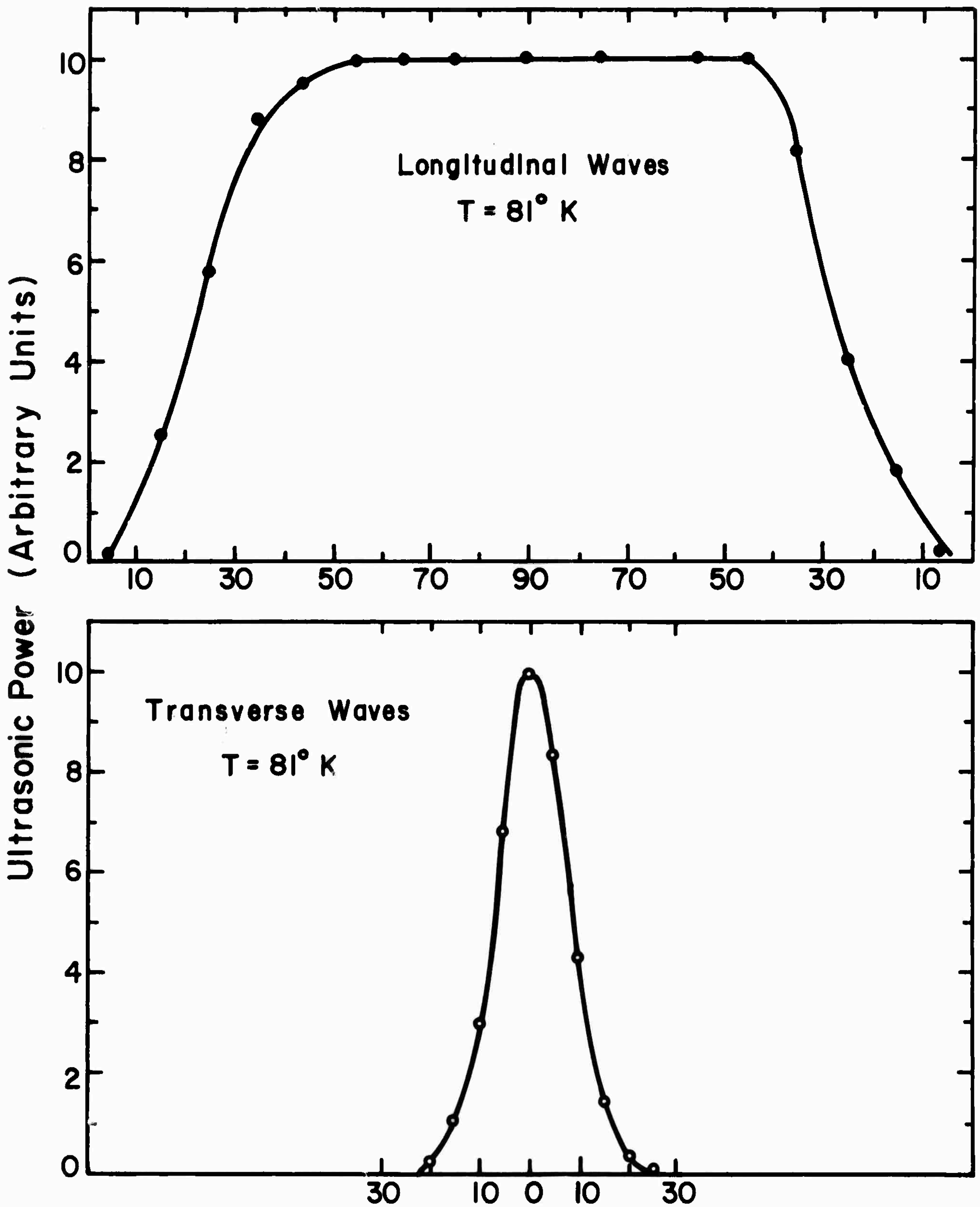
Figure 5. Dependence of ultrasonic generation in dysprosium thin films on applied magnetic field strength. The frequency is 1,000 Mhz, and the field is applied parallel to the plane of the film.


Longitudinal Waves
H-Parallel
T= 81° K
Ultrasonic Power (Arbitrary Units)
10
8
6
4
2
3
4
6
8
10
12
14
16
18
H- kOe

with the field perpendicular to the film at various temperatures and at a frequency of 1.0 GHz, it is seen that the ultrasonic amplitude increases sharply with field strength, showing only a slight tendency to level off at the highest field available, 20 kG. This behavior is obtained at all temperatures in the ferromagnetic range for dysprosium (below 85 K). In Figure 5, by contrast, which shows the results obtained with the field parallel to the film, it is seen that a broad maximum in the generation occurs in the range of 6-8 kG. It should also be noted that only shear waves are generated in the case of the perpendicular field, whereas only longitudinal waves are generated in the parallel-field case. At a frequency of 9.3 GHz, ultrasonic generation could only be observed with the field perpendicular to the film, and its field dependence was identical to that observed at 1.0 GHz. The generation of the longitudinal waves at 1.0 GHz was relatively insensitive to the direction of the field, as shown in Figure 6, but the transverse-wave generation could only be obtained with the direction of the field within approximately 20° from the normal to the film. The intensity of the ultrasonic waves observed at 1.0 GHz was an order of magnitude greater than can be obtained with nickel or permalloy films, but it was of the same magnitude as that which can be obtained with piezoelectric semiconductor transducers such as cadmium sulfide. At 9.3 GHz, however, the ultrasonic intensity

Figure 6. Dependence of ultrasonic generation in dysprosium thin films on the direction of the applied field at 1,000 MHz.

Angular Dependence



Field Direction With Respect To Film Normal – Degrees

was perhaps 1,000 times as large as that which has been observed with quartz transducers at this frequency under the same conditions of excitation, namely, with the transducer placed inside a simple rectangular cavity. The use of cavities which concentrate the rf electromagnetic fields should improve the efficiency of ultrasonic generation by means of magnetostriction by a factor as large as 100.

The nature of the ultrasonic generation using thin films of dysprosium can be understood only partially at this time. The continuing increase of the intensity of the transverse waves as a function of field strength is probably due in part to the large demagnetizing factor which exists when the field is perpendicular to the film. At present, with the field limitation of 20 kG it is not known where the maximum intensity occurs, but a superconducting magnet capable of producing fields as high as 50 kG is being readied for operation, and it will undoubtedly permit the determination of the full field dependence of the ultrasonic generation. All that can be said at present concerning the field dependence is that the polycrystalline film behaves more or less as an isotropic film in which a very broad ferromagnetic resonance is excited, accompanied by a resonant generation of ultrasonic waves. On the other hand, the longitudinal-wave resonance shown in Figure 4, occurring in the niehgobrhood of 6-8 kG cannot be explained on

the basis of a uniform-precession ferromagnetic resonance, and further work will be required, probably with single-crystal transducers before this resonance can be understood. It is expected that all these results obtained with dysprosium will be understood in a much more satisfactory manner by the completion of this program.

Gadolinium: Gadolinium, which exhibits very little magnetocrystalline anisotropy, is much simpler to interpret than is dysprosium. However, the small degree of anisotropy also has the consequence that the magnetostriction in gadolinium is much smaller than it is in the other magnetically ordered rare earths. Nevertheless, since gadolinium remains ferromagnetic up to a Curie temperature of 293 K, and since its magnetostriction is considerably larger than that of any of the iron-group elements or alloys, it has also been investigated as a magnetostrictive transducer. Typical results are shown in Figures 7 and 8. In both these figures, the field dependence of the ultrasonic amplitude is shown, and in both figures the results are given for transverse waves with the field perpendicular to the plane of the film. In Figure 7 results are given for a frequency of 800 MHz, and in Figure 8 the frequency is 9.3 GHz. Both results are explainable in terms of a simple ferromagnetic resonance accompanied by a resonant generation of ultrasonic waves. The position of the resonant peak in both cases is consistent with known single-crystal properties, since

Figure 7. Dependence of ultrasonic generation in gadolinium thin films on applied magnetic field strength. The frequency is 800 MHz, and the field is perpendicular to the plane of the film.

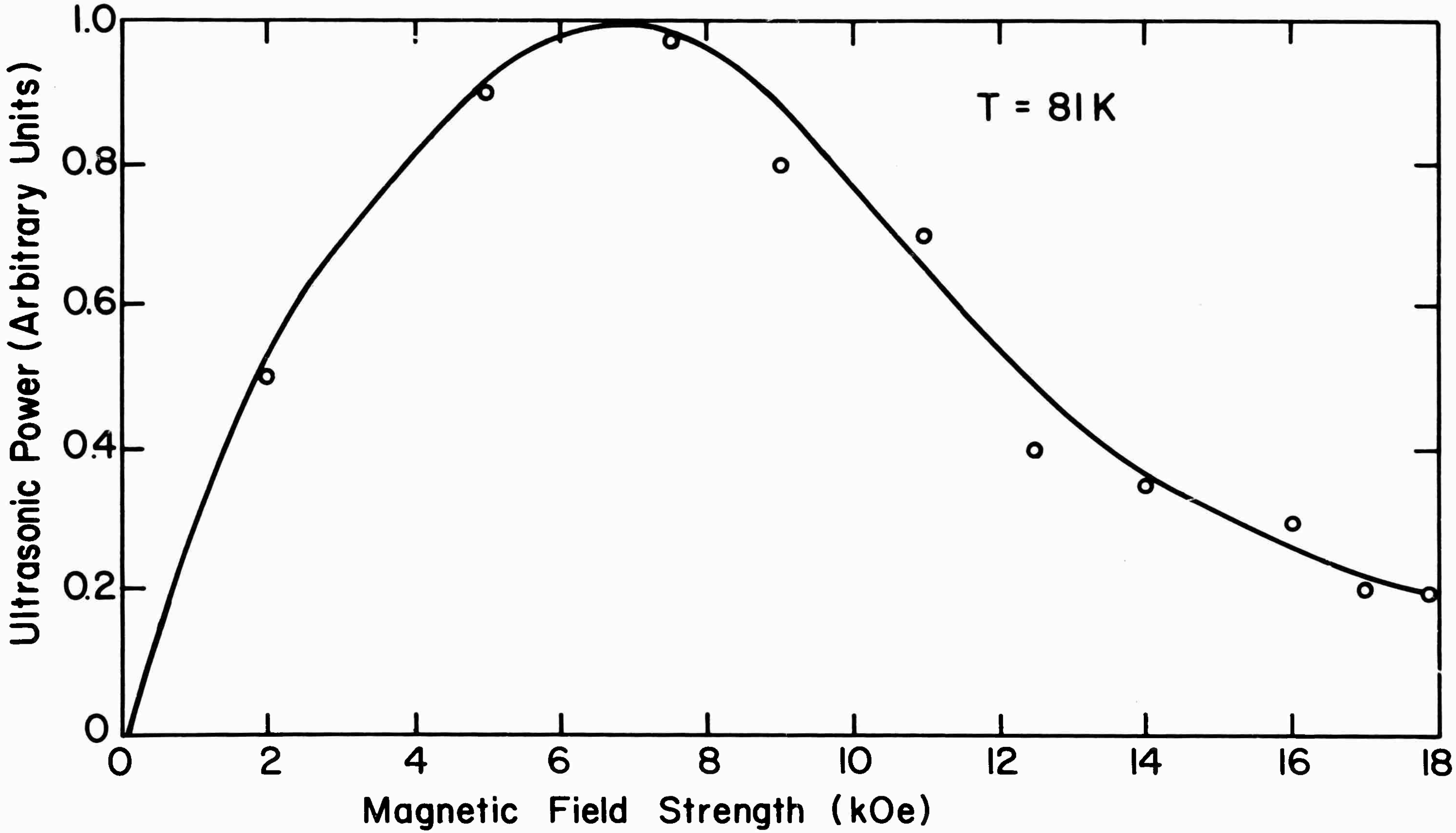
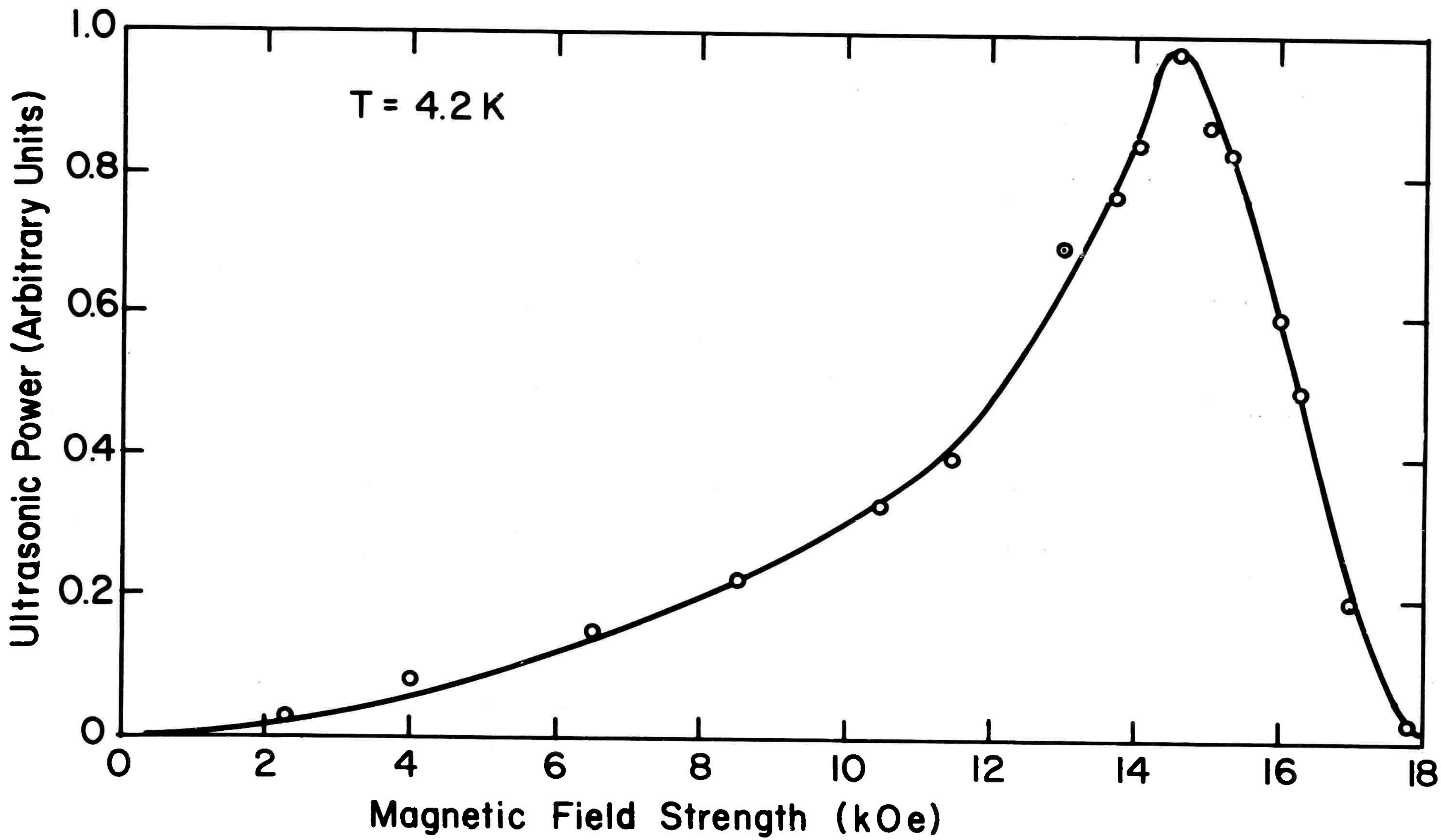

T = 81 K
Ultrasonic Power (Arbitrary Units)
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
16
18
Magnetic Field Strength (kOe)

Figure 8. Dependence of ultrasonic generation in gadolinium thin films on applied magnetic field strength. The frequency is 9.3 GHz, and the field is perpendicular to the plane of the film.



T = 4.2 K
Ultrasonic Power (Arbitrary Units)
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
16
18
Magnetic Field Strength (kOe)

anisotropy plays only a small role, determining primarily the width of the resonant peaks.

A surprising feature of the experimental results is that the ultrasonic intensity for gadolinium is approximately equal to that for dysprosium, despite the ten-fold smaller magnetostriction of gadolinium. This result implies that the polycrystalline nature of the films is much more effective in reducing the magnetostriction of a highly anisotropic material such as dysprosium than it is for the relatively isotropic gadolinium, as expected.

Because it is easily bonded to a nonmagnetic substrate, work is in progress to investigate ultrasonic generation in a single-crystal gadolinium transducer. It is expected that resonant generation will again be observed in this case, but that the resonance will be much narrower and much more intense.

Holmium and Erbium: Only very limited results have been obtained with these materials. Ultrasonic generation has been observed, but because of the relatively low magnetic-ordering temperatures of these elements no attempt has been made as yet to investigate thoroughly ultrasonic generation, although alloys of these highly magnetostrictive materials with other rare earths should prove interesting.

2. Ultrasonic Wave Propagation in Single-Crystal Rare Earths

A very valuable method of investigating the magnetoelastic properties of solids is the study of the propagation of ultrasonic waves through the solid, observing the effects of an applied magnetic field on both the attenuation of the ultrasonic waves and on their velocity[3-5]. The magnetoelastic coupling in a magnetically ordered solid normally leads to very striking changes in both attenuation and velocity as the applied magnetic field is varied through a range where magnetic resonance occurs at the ultrasonic frequency or where magnetic phase changes occur. Even in the case of paramagnetic solids the magnetoelastic interaction can lead to enormous changes in the propagation characteristics of high-frequency ultrasonic waves[6]. In the case of the rare earths, in particular, the study of ultrasonic propagation is of some interest because accurate measurement of the ultrasonic-wave velocity permits a determination of the elastic constants, which have been determined only for one or two of the pure rare earths. The elastic constants enter into the determination of the magnetostrictive properties of a solid, so that the knowledge of these constants for the materials of interest to this research program is extremely desirable. Consequently, a detailed investigation of elastic-wave propagation in terbium, one of the most strongly magnetostrictive

of the rare earths, has been carried out at a frequency of 20 MHz. The results of this investigation have proved to be quite interesting, both from a fundamental point of view and from a more practical point of view. Useful information about the strength and general nature of the magnetoelastic interaction in terbium has been obtained, and the results also indicate a possible technological application which may find a number of uses. The results obtained with terbium have been so interesting that it is planned to extend this work to include also dysprosium, holmium, erbium, and gadolinium.

Magnetic measurements[7] and neutron-diffraction studies[8] have shown that terbium is paramagnetic above a temperature of 229 K. In the range from 221 K to 229 K, however, it is antiferromagnetic, with the magnetic moment of each basal plane lying in the basal plane but with the moments of successive planes along the c-axis being rotated to give a helical magnetic structure. The application of a small magnetic field (less than 1 kG) induces a transformation of this helical structure to a ferromagnetic alignment of the magnetic moments. Below 221 K terbium is ferromagnetic even in the absence of an applied magnetic field, and the magnetic moments are all parallel to the basal plane, with a small anisotropy tending to align the magnetization along the b-axis ($[10\bar{1}0]$ direction). Because of these varied magnetic phases which occur

in different temperature ranges, and because the magnetoelastic coupling in terbium is extremely large, as evidenced by its large magnetostriction, the wide range of magnetic structures which can occur at different temperatures and applied fields leads to a number of very interesting effects on the attenuation and dispersion of ultrasonic waves at all frequencies. A thorough study of these effects can lead to an improved understanding of the magnetoelastic coupling. The work reported here has yielded many interesting results, but it has not yet been possible to work with extremely thin samples, which, because of their small demagnetizing factors, would permit a complete interpretation of these results. Consequently, the interpretations given here are to be considered preliminary in most respects.

The results obtained to the present which are of greatest interest concern the effects of applied magnetic fields on the propagation of 20-MHz longitudinal ultrasonic waves propagated along a basal-plane direction (b-axis) and along the hexagonal axis of the hcp structure of single-crystal terbium. The specimen was in the form of a cylinder 6 mm long and 6 mm in diameter, with the cylindrical axis parallel to the direction of propagation. Ultrasonic waves were generated and detected using apparatus normally employed for pulse-echo measurements of ultrasonic velocities. The magnetic field strength could be varied from zero

to 17 kG, and its direction could be rotated in a plane perpendicular to the axis of propagation of the ultrasonic waves. The sample dimensions were far from the optimum values which would permit the simplest interpretation of the results in the presence of a magnetic field, since the demagnetization effects are nonuniform in such a sample, and the effective demagnetizing factor is large in every direction. It is thus difficult to determine the internal field within the specimen with any accuracy for such a sample, and the internal field is in any event nonuniform, even when the sample is completely saturated. Since equipment was already available for the ultrasonic measurements which demanded this unfavorable sample geometry, it was felt that these difficulties were not sufficiently important to require the redesign of the ultrasonic part of the experiment. Nevertheless, thin, disk-shaped samples with uniform internal fields and small demagnetizing factors will be employed when possible in future work. The specimen was placed in a cryostat permitting operation at any temperature in the range 1.5 K to 300 K, with a temperature stability at any point within this range of ± 0.1 K.

Although the results which have been obtained to date include an accurate measurement of most of the elastic constants of terbium, this report will only include a description and discussion of those results which have a direct bearing on the magnetoelastic

interaction. The results to be discussed can be divided into two parts: those concerning wave propagation in the basal plane, which is the direction of the magnetization in both the helical and ferromagnetic phases, and those involving propagation along the hexagonal c-axis, perpendicular to the magnetization.

(a) <u>Propagation in Basal Plane (Longitudinal Waves along b-Axis)</u>

The principal experimental results are summarized in Figures 9-11. In the absence of an applied magnetic field, Figure 9, curve I, the attenuation of the waves exhibited a sharp minimum near the paramagnetic-helimagnetic transition temperature, T_N = 229 K. Below this temperature, the attenuation rose sharply, becoming so large at and below the helimagnetic-ferromagnetic transition temperature, T_C = 221 K, that the ultrasonic echoes disappeared completely. This behavior is quite different from that observed in the case of longitudinal waves propagated along the c-axis, as discussed below. In the presence of a strong magnetic field, Figure 9, curve II, the temperature dependence of the attenuation was strongly changed. For a field of 15 kG along the a-axis in the basal plane, the paramagnetic attenuation increased moderately with decreasing temperature, reaching a maximum at T = 245 K, well above T_N. As the temperature was further decreased, the attenuation decreased sharply, reaching a broad minimum near T_C. A simple

__Figure 9__. Temperature dependence of ultrasonic attenuation in terbium single crystals; longitudinal waves at 20 MHz propagating along crystallographic b-axis. Curve I applies in the case of no magnetic field, while for Curve II a magnetic field of 15 kG was applied along the crystallographic a-axis.

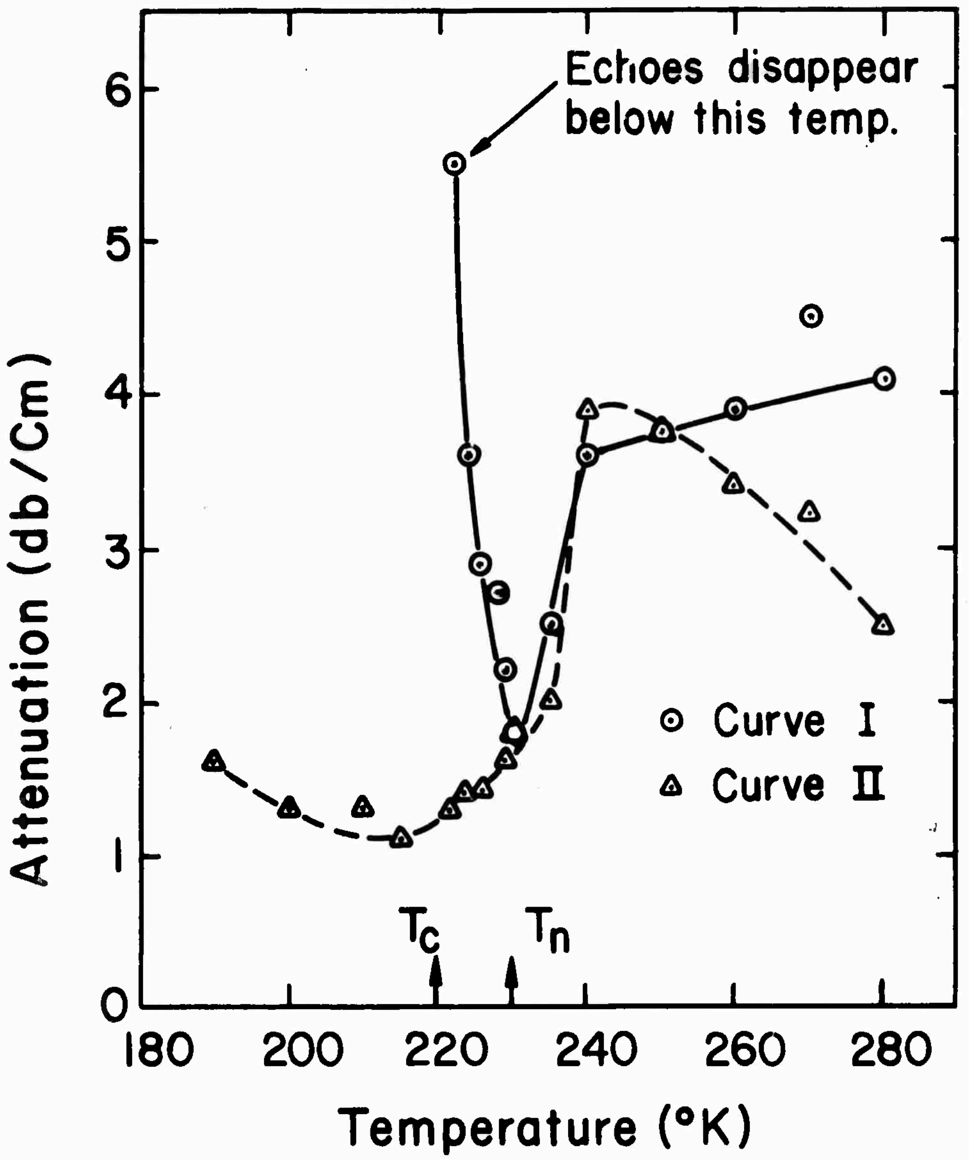
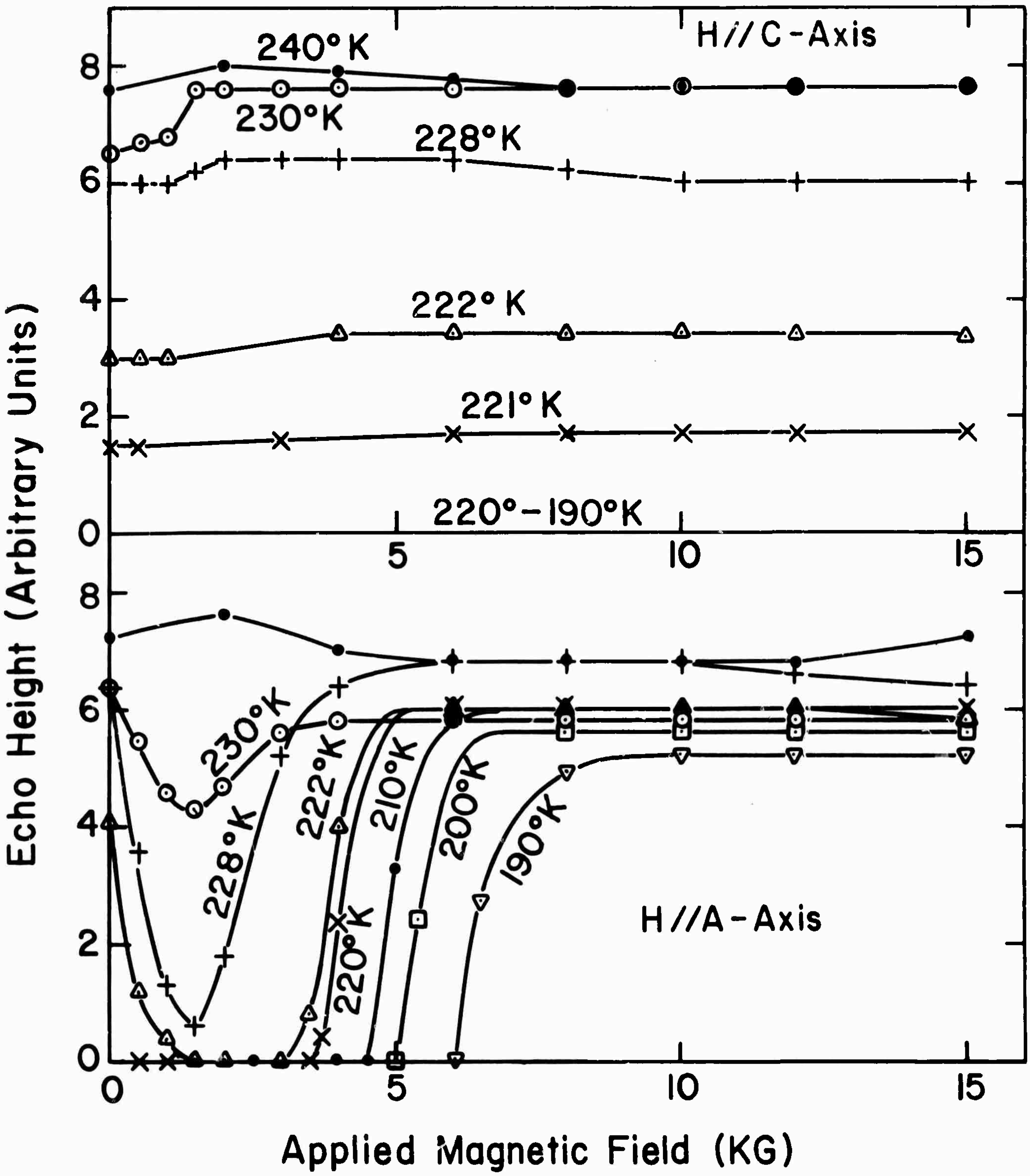
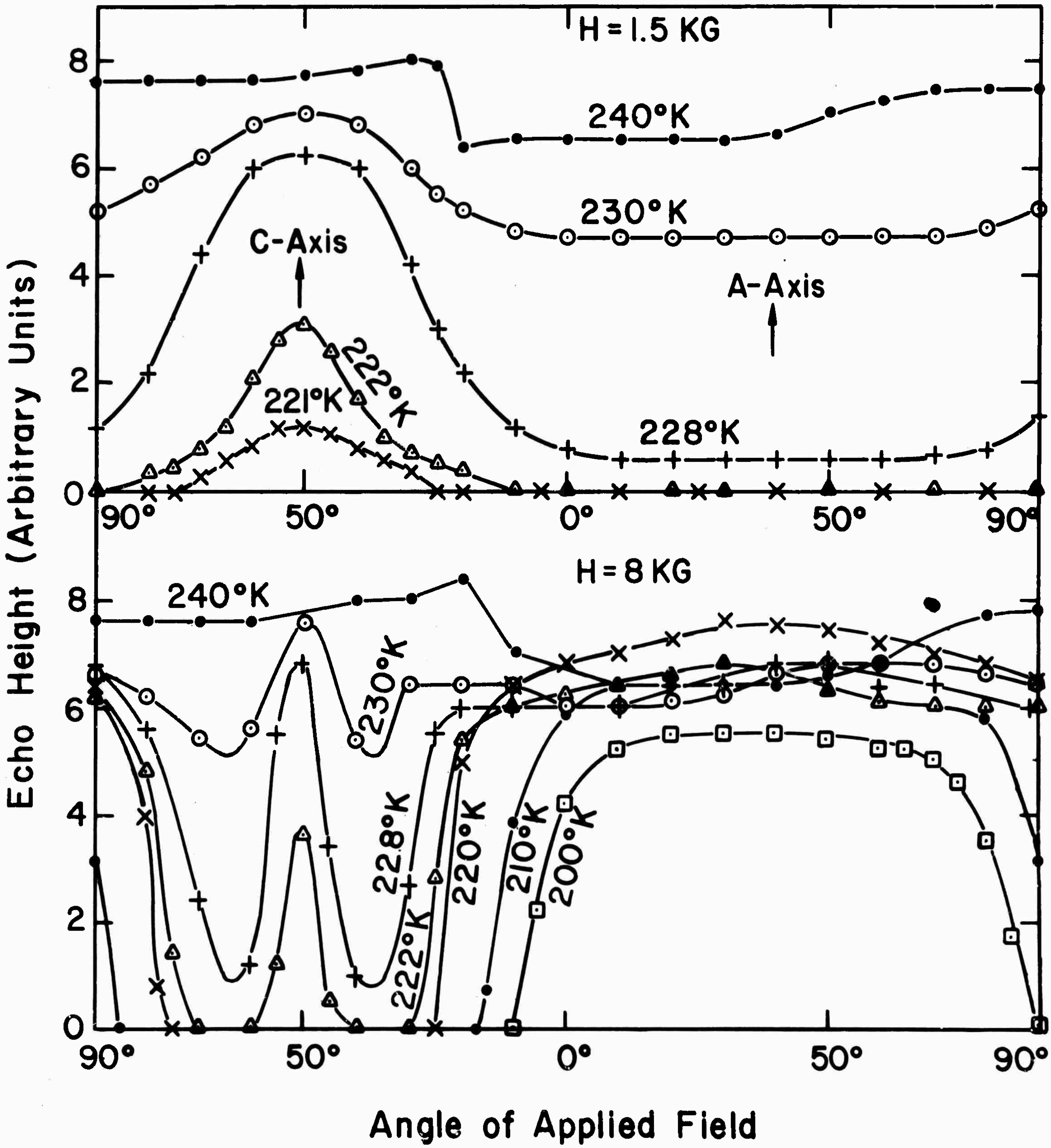

Echoes disappear below this temp.
Attenuation (db/Cm)
0
1
2
3
4
5
6
180
200
220
240
260
280
Temperature (°K)
Tc
Tn
Curve I
Curve II

Figure 10. Field dependence of ultrasonic amplitude in terbium single crystals at various temperatures. The frequency is 20 MHz, and the waves are longitudinally polarized along the crystallographic b-axis.



H//C-Axis
240° K
230°K
228°K
222° K
221° K
220°-190°K
230°K
228°K
222°K
220°K
210°K
200°K
190°K
H//A-Axis
Echo Height (Arbitrary Units)
Applied Magnetic Field (KG)
0
2
4
6
8
5
10
15

Figure 11. Dependence of ultrasonic amplitude in terbium single crystals on the direction of the applied magnetic field; longitudinal waves propagating along the crystallographic b-axis at 20 MHz.


H = 1.5 KG
240°K
230°K
C-Axis
A-Axis
222°K
221°K
228°K
90°
50°
0°
50°
90°
H = 8 KG
240°K
230°K
228°K
222°K
220°K
210°K
200°K
0
2
4
6
8
Echo Height (Arbitrary Units)
Angle of Applied Field

qualitative interpretation of the striking reduction in the ferromagnetic attenuation under the application of a large magnetic field is the following: The large ferromagnetic attenuation in the absence of an applied field is due to a strong interaction between the elastic ultrasonic waves and spin waves of the same frequency and approximately the same wavelength. The application of a strong magnetic field shifts the spin-wave frequencies to much higher values, thereby suppressing most of the magnetoelastic interaction.

Perhaps a more interesting and instructive way to view the results of the application of a magnetic field is shown in Figures 10 and 11, in which isotherms at various temperatures in the range of interest are shown, illustrating the field-dependence of the amplitude of the first ultrasonic echo (the only echo observable in regions of high attenuation; even this echo was not observable at the highest attenuation encountered). In Figure 11, the dependence of the echo amplitude on field strength for two different field orientations is shown. For the field parallel to the hexagonal c-axis, there is very little dependence of the echo amplitude on field strength. This is to be expected, since the magnetization is constrained by the very strong uniaxial magnetocrystalline anisotropy to lie in the basal plane. Consequently, an applied magnetic field along the c-axis has little effect on the magnetic ordering and,

particularly, on the spin-wave frequencies. Only at values of the field strength comparable to the effective anisotropy field, approximately 100-200 kG, would any significant effect be expected with the field directed parallel to the c-axis.

For the case in which the field is directed along the a-axis, however, a very strong field dependence was observed at temperatures below T_N. At temperatures between T_N and T_C, the initial echo amplitude at zero applied field, where the specimen is helimagnetic, was finite, although it decreased at the temperature was reduced. In all cases in this temperature range, the initial echo amplitude decreased sharply with increasing field, reaching a minimum (which was undetectably small at temperatures very close to T_C) at a value of the applied field sufficient to induce the phase transition to the ferromagnetic state. As the field was increased further, the amplitude increased from its minimum value, quickly reaching a field-independent value in some cases somewhat greater than the initial (zero-field) value. At temperatures below T_C, the initial echo amplitude at zero field was undetectably small, but the echo reappeared at fields above a critical value which increased with decreasing temperature.

The field dependence of the echo amplitude in the range $T_C < T < T_N$ can be interpreted qualitatively in the following way. At zero applied field, the specimen is helimagnetic, and the

magnetoelastic coupling, whose strength is proportional to the square of the magnetization, is very small. As the magnetic field is applied, the rather large helimagnetic susceptibility leads to an induced magnetization, accompanied by an increased magnetoelastic coupling. Since there are always low-frequency spin-wave modes present while the magnetic structure is helimagnetic (even distorted)[9], this increased magnetoelastic coupling leads to an absorption of elastic energy by the spin waves at the ultrasonic frequency and the resulting observed attenuation. As the field is increased further, so that the specimen becomes ferromagnetic, the attenuation continues to increase, since there are still low-frequency spin-wave modes at fields near the helimagnetic-ferromagnetic transition. At still higher field values, however, the spin-wave frequencies are raised out of the range of the ultrasonic frequency, so that, despite the large magnetoelastic coupling, the interaction between spin waves and elastic waves is suppressed, and the attenuation decreases.

The curves of Figure 11 show the dependence of echo amplitude on the direction of the applied field for two different field values and several different temperatures. The principal significance of these results is the fact that it is only the component of the field parallel to the basal plane which is effective in modifying the attenuation appreciably. Rotation of the field

direction from the c-axis to the a-axis reproduces almost exactly the field dependences shown in Figure 10, if the angular variation of the basal-plane component of the field is taken into account. One anomalous feature of the curves shown in this figure is the sudden small jump in the echo amplitude at a temperature of 240 K, well above T_N, when the field direction lay approximately midway between the a-axis and the c-axis. The significance of this effect is not known at this time.

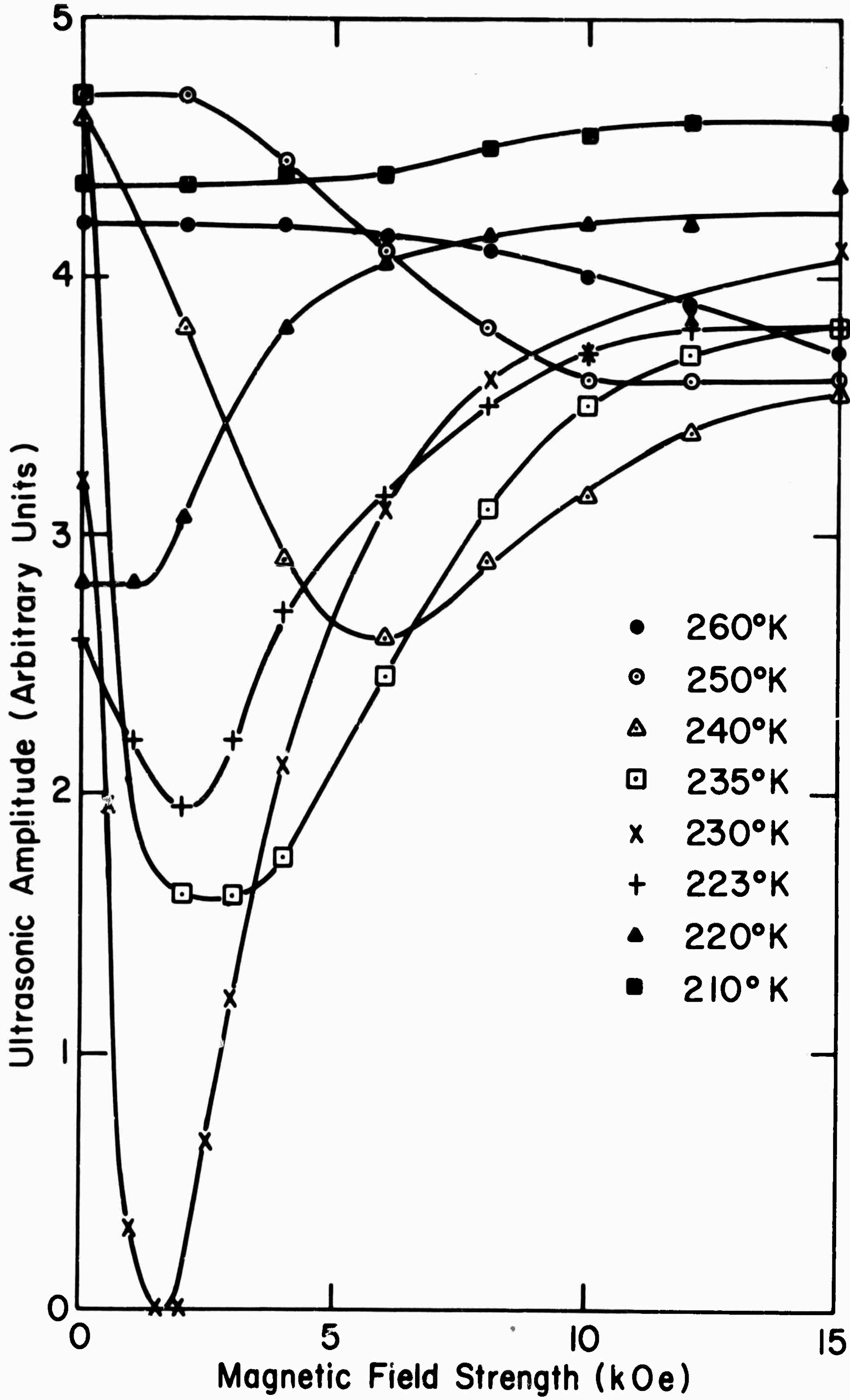
The most interesting feature of the results reported for this case, in which longitudinal elastic waves are propagated along the b-axis in the basal plane, is the extremely sharply field-dependent ultrasonic attenuation occurring at temperatures below T_N. If the demagnetization factor, which is quite large for the specimen geometry employed in this work, is taken into account, then the field dependence, expressed in terms of the internal field, is exceptionally sharp. A change in internal field as small as 10 G can produce an order-of-magnitude change in the attenuation. There are two major points of interest concerning this strong field dependence of the attenuation. First, the possibility of constructing a simple ultrasonic modulator or switch requiring very little switching or modulating power can easily be seen. If a sample in the form of a thin disk is employed, then the necessary change in internal field can be achieved with only a small change in

the applied field. Devices based on this effect should find useful applications in the fields of computing, communications, and signal processing in general. Second, from the standpoint of the primary goal of this program, since the magnetoelastic coupling is reciprocal, the application of small oscillating magnetic fields to a terbium specimen should lead to a highly efficient conversion of electromagnetic energy into elastic-wave energy. Thus, single-crystal terbium should prove to be a material worth investigating as a high-intensity transducer. Its required operation at cryogenic temperatures may, perhaps, not be a serious drawback, since the temperatures of interest are only a few degrees below room temperature, and can be reached with readily available coolants.

(b) Propagation along Hexagonal Axis (Longitudinal Waves)

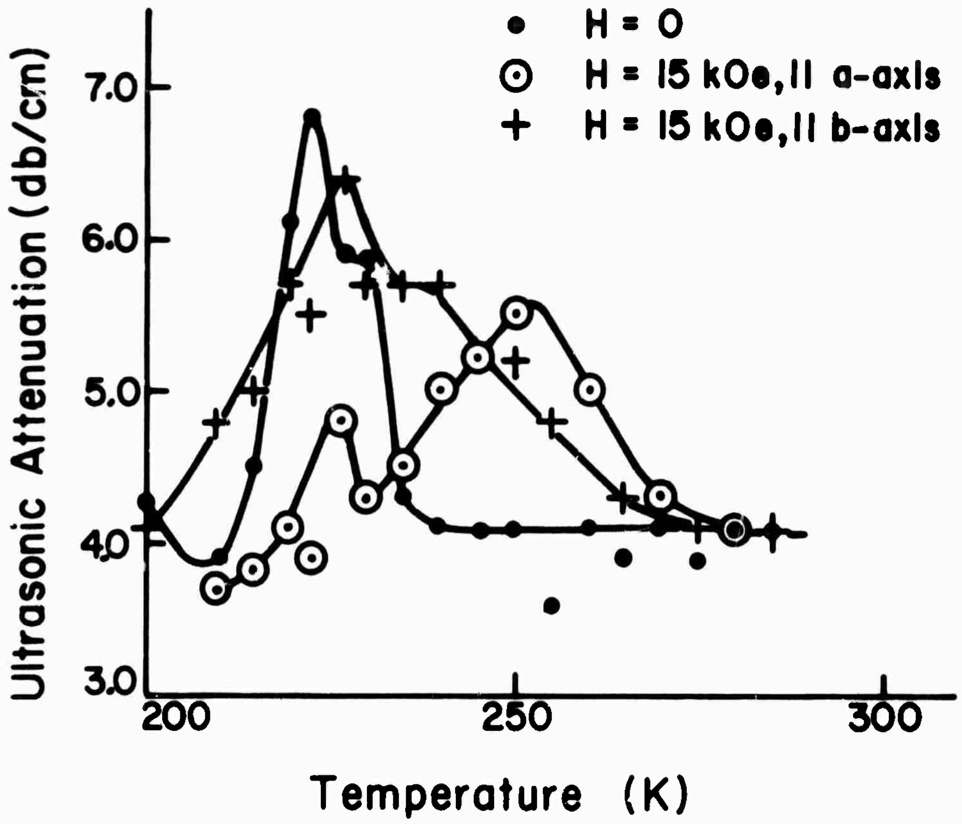
For wave propagation along the c-axis, the results are shown in Figures 12-14. In this case, there are certain qualitative similarities to the previous case, but there are interesting differences, both qualitative and quantitative. The temperature dependence of the attenuation with and without the application of a magnetic field in the basal plane is shown in Figure 12. In the absence of an applied field, there is a peak attenuation at T_C, but the attenuation falls to lower values at lower temperatures, in contrast to the case of propagation along the b-axis. There is a

Figure 12. Temperature dependence of ultrasonic attenuation in terbium single crystals; longitudinal waves at 20 MHz propagating along hexagonal c-axis; with and without applied magnetic field.



5
4
3
2
1
0
0
5
10
15
Ultrasonic Amplitude (Arbitrary Units)
Magnetic Field Strength (kOe)
260°K
250°K
240°K
235°K
230°K
223°K
220°K
210°K

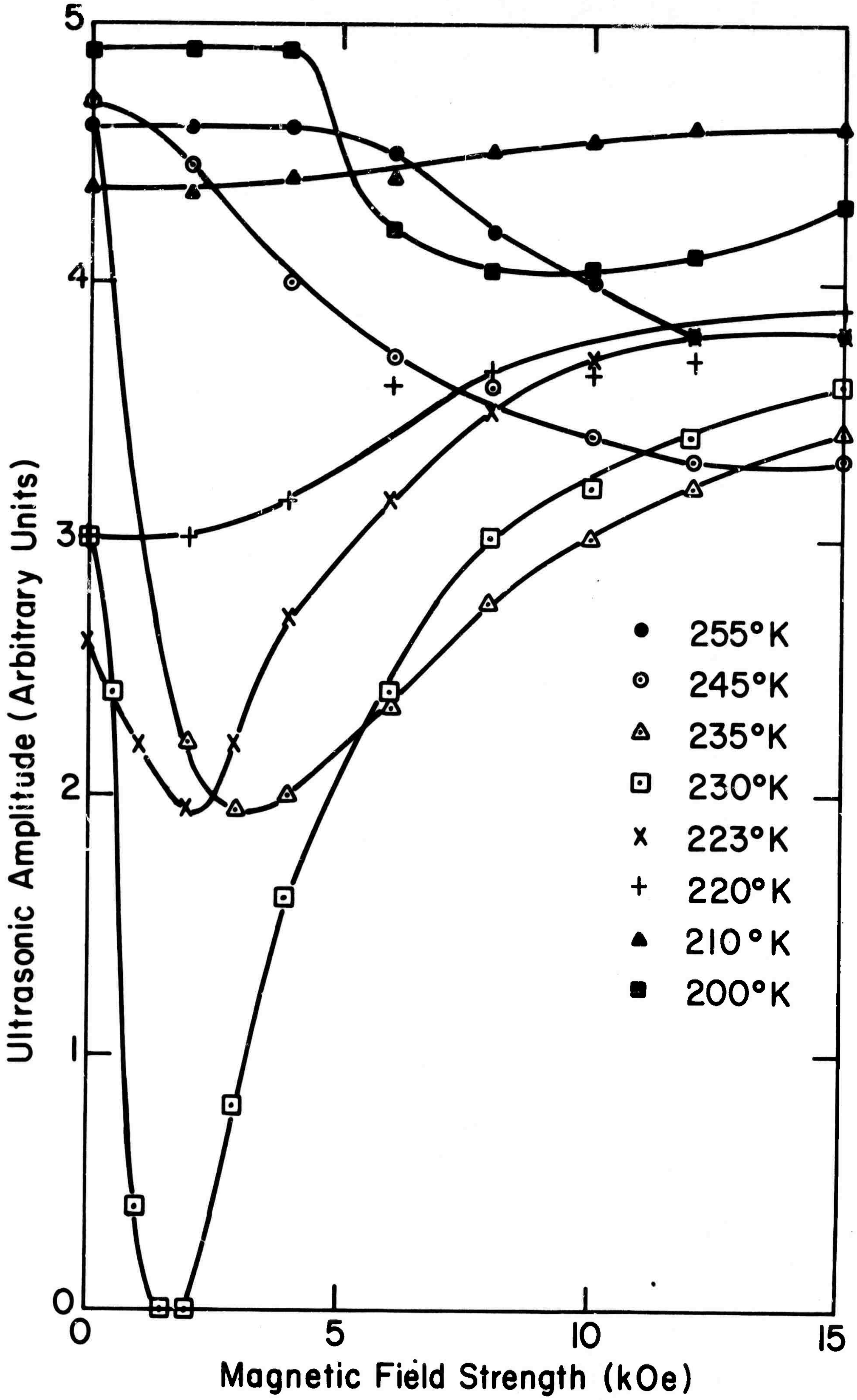
<u>Figure 13</u>. Field dependence of ultrasonic amplitude in terbium single crystals at various temperatures; longitudinal waves at 20 MHz propagating along crystallographic c-axis; field along a-axis.



H = 0
H = 15 kOe, ll a-axis
H = 15 kOe, ll b-axis
Ultrasonic Attenuation (db/cm)
7.0
6.0
5.0
4.0
3.0
200
250
300
Temperature (K)

Figure 14. Field dependence of ultrasonic amplitude in terbium single crystals at various temperatures; longitudinal waves at 20 MHz propagating along crystallographic c-axis; field along b-axis.

55



Ultrasonic Amplitude (Arbitrary Units)
Magnetic Field Strength (kOe)
0
1
2
3
4
5
0
5
10
15
255°K
245°K
235°K
230°K
223°K
220°K
210°K
200°K

shoulder on the curve at approximately T_N. The application of a large magnetic field separates the curve into two peaks, although both are shifted to higher temperatures. In fact, with the field parallel to the a-axis, the higher-temperature peak occurs at a temperature of 250 K, well into the normally paramagnetic region, whereas the lower-temperature peak occurs at approximately T_N. The effect of the field is not nearly so pronounced when the field lies along the b-axis, and this high degree of basal-plane anisotropy is quite surprising, since the basal-plane anisotropy with respect to most other magnetic properties of terbium is rather small.

The field dependence of the echo amplitude at constant temperature is shown in Figures 13 and 14. The most interesting features of the curves shown in these two figures concerns the field dependence of the echo amplitude at a temperature very close to T_N, namely 230 K. There is a very sharp minimum in the amplitude at an applied field of approximately 1.5 kG, corresponding to an internal field, when demagnetization is taken into account, of less than 100 G. Thus, in this case as well as the previous one, the same potential applications can be seen, although the field-dependent attenuation is not nearly so strongly varying in this case as it is when the waves are propagated along the b-axis.

Work is continuing on terbium, at higher fields and lower temperatures. Furthermore, an experiment utilizing terbium as an ultrasonic transducer is under way.

3. Single-Crystal Growth of Rare-Earth Elements, Alloys and Compounds

Although it is now possible to obtain good single-crystal specimens of some of the rare earths at reasonable cost, delivery times are long, the quality of the crystals is rather variable in several respects, and, if large quantities of rare-earth materials are to be investigated, the cost, some one hundred times the cost of high-purity polycrystalline materials, rapidly becomes prohibitive. When alloys of one rare earth with another are considered, commercial sources are still available, but the cost is much higher than in the case of the pure rare earths, and the composition of the alloys does not always meet specifications. Delivery times in excess of one year are not uncommon in the case of alloys. For other materials containing rare earths, such as the very interesting rare-earth-cobalt intermetallic compounds, which are apparently highly magnetostrictive, while at the same time they exhibit rather high Curie temperatures, not only are single-crystal specimens commercially unavailable, but polycrystalline materials are being produced in only a few laboratories. Yet in all these cases the high degree of magnetic anisotropy normally associated with the rare earths makes the study of the properties of single-crystal specimens highly desirable.

Because of the need for single-crystal specimens and because of the difficulties discussed above in obtaining suitable specimens, it was originally planned to construct apparatus for the growth of the specimens to be used in this program. Although the only detailed reports concerning the growth of single-crystal rare-earth elements and alloys have been concerned with the strain-annealing method of growth[10], commercially grown crystals are produced reliably by means of floating-zone melting. Since the strain-annealing method does not yield large crystals consistently, and since the zone-refining method permits the growth of long oriented crystals suitable for the type of research of interest in this program, the latter method was chosen in the work reported here.

A major problem in any attempt to zone-melt materials rich in the rare-earth elements is the fact that, although the melting points of the rare earths are quite reasonable (1200-1500°C), the vapor pressures of these elements are all quite high at the melting point, of the order of one Torr. Consequently, electron-beam zone melting is impossible. The high vacuum required in order to permit the use of electron-bombardment heating also permits the rapid evaporation of the rare-earth material. The major effort in this program has, therefore, been directed toward zone melting by means of rf induction heating of the sample in an inert atmosphere. The inert-gas atmosphere, at normal atmospheric pressure, inhibits the

evaporation of the rare-earth material without introducing appreciable contamination during the growth process.

Initial attempts at growing crystals of relatively pure dysprosium yielded zone-refined rods of diameter approximately 6 mm and length 50 mm, normally containing two or three large single-crystal grains, randomly oriented. No seed crystal was employed. In the early attempts, it was not possible to investigate the dependence of grain size on the rate of growth or even on such a simple parameter as the number of zone passes because the rf induction generator employed for this work was an industrial 10-kW unit with no means for accurate control of the rf level. Consequently, only one rather quick pass could be made in most cases, while the rf level was regulated manually by the operator. Nevertheless, the results were encouraging enough that it was decided to modify the generator to permit feedback regulation of the temperature of the floating melted zone, in order that multiple passes could be made at any desired speed.

During the six-month period covered by this report, work was directed toward the construction of a mechanical system for coupling the rf energy into the specimen inside a bell-jar system within which the atmosphere could be controlled. The bell-jar and crystal-growing apparatus are attached to a high-speed vacuum system which permits outgassing the sample and all associated

equipment under high vacuum before beginning the zone-melting procedure. After thorough outgassing, high-purity helium, obtained in the form of the gas evaporating from a liquid-helium reservoir, is admitted to the bell jar and maintained at approximately atmospheric pressure. The zone-melting procedure then commences. The apparatus is illustrated in Figure 15.

In addition, as mentioned above, it was necessary to design and construct a control system for the rf generator which could maintain the temperature of the melted zone at any desired value indefinitely. It was decided to employ an optical sensor for detection of the zone temperature and, by means of a feedback control system, to regulate the rf output power of the generator in such a way as to maintain a constant temperature. The need for good control of the zone temperature is illustrated by Figure 16, in which the effects of temperature variation during zone melting are shown. The sample is dysprosium, and an attempt to grow a single crystal was made using manual regulation of the zone temperature. Sudden fluctuations in the rf output power lead to changes in the length of the molten zone before the operator can make a correction to the rf level, with the results that large changes in the diameter of the sample rod occur. In extreme cases, the zone may become so long that surface tension will no longer support the zone against the force of gravity, with the result that the molten zone falls apart.

Figure 15. Photographic view of apparatus for growth of aingle crystals of rare-earth materials by induction zone refining; bell jar removed.

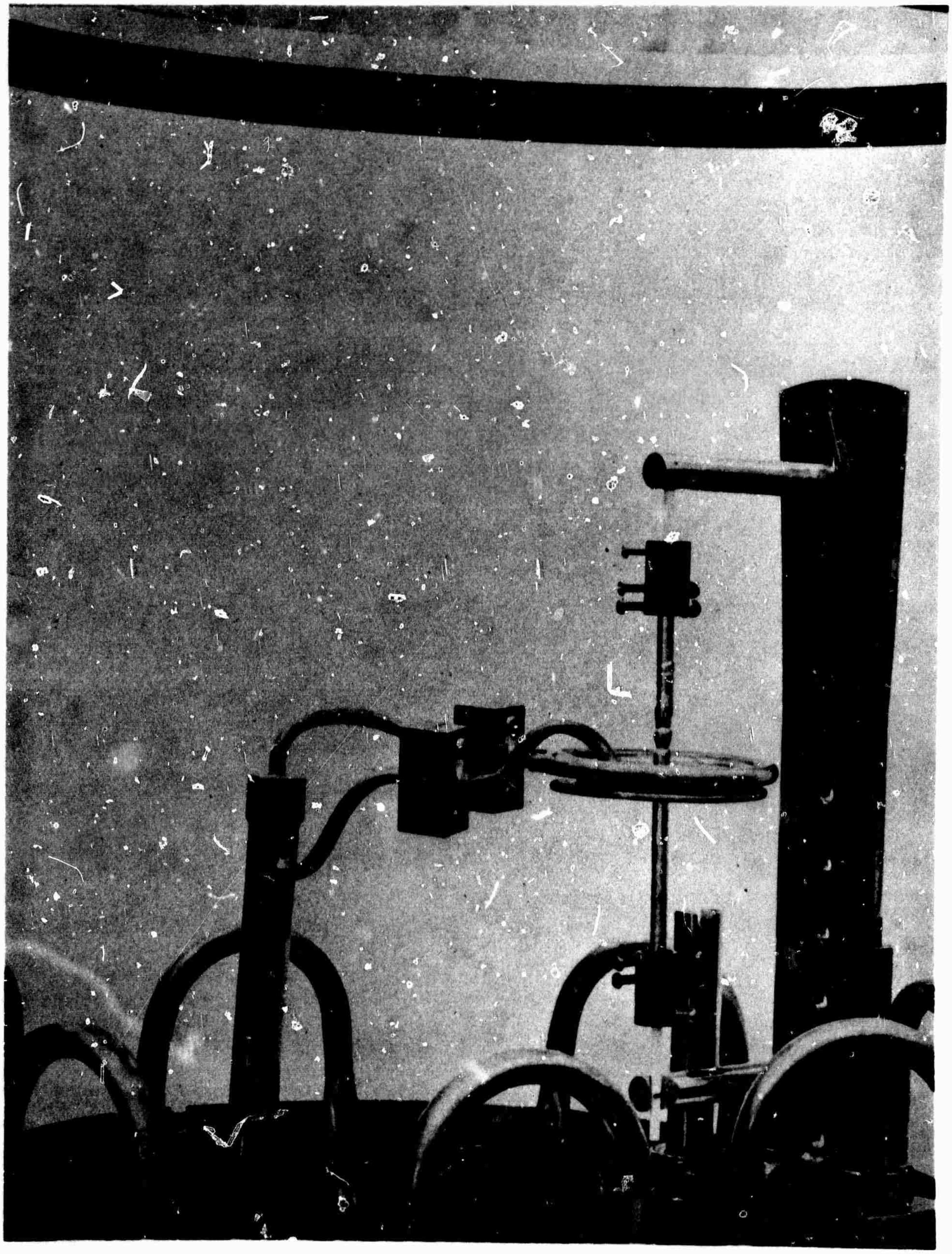
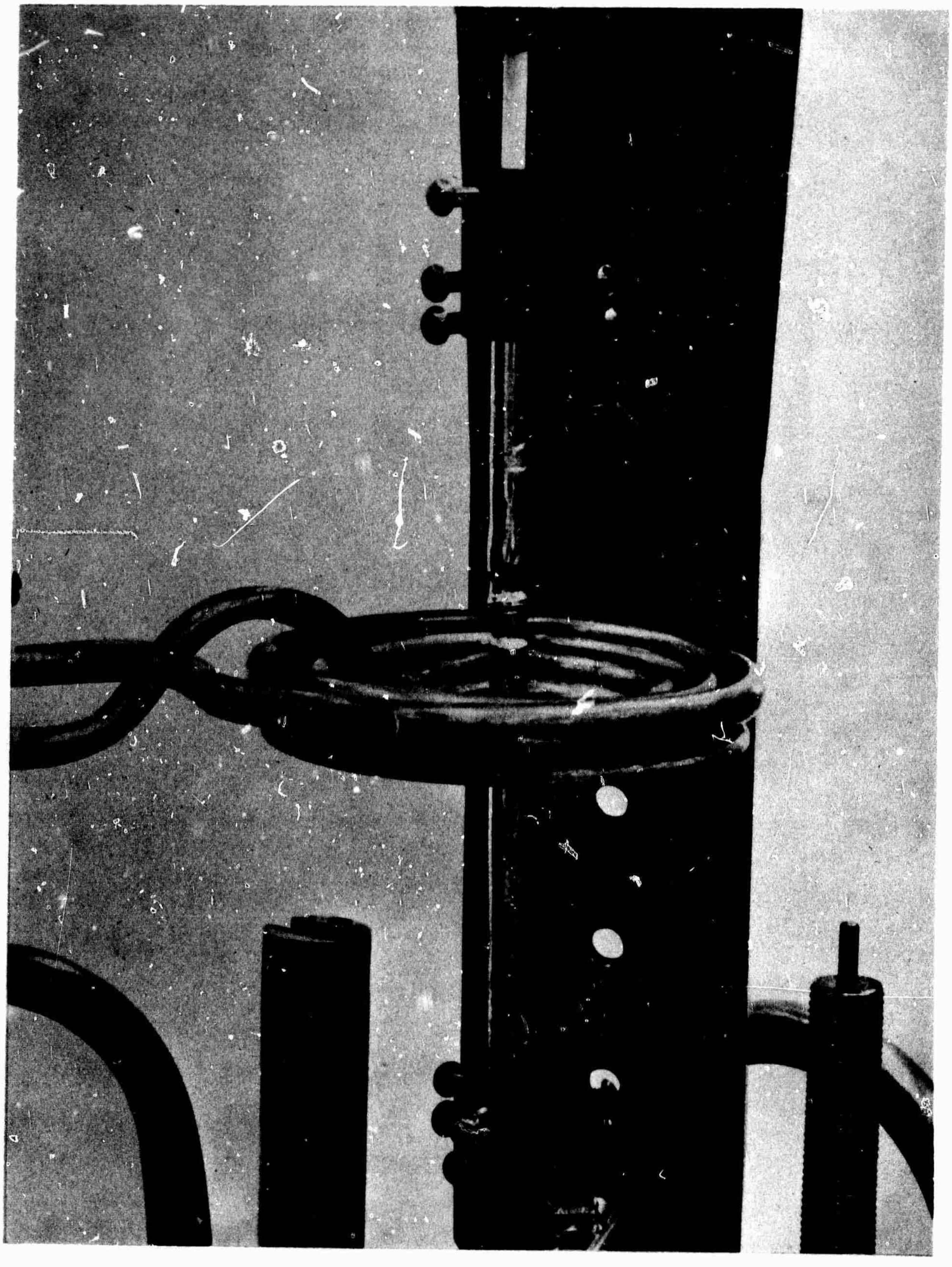


Figure 16. View of rare-earth sample after zone-refining pass with manual regulation of output level of rf generator.



In the attempt to provide an electronic control system for the rf generator, which is an industrial unit not designed for precise control, it was found that no straightforward electronic method of regulation could be made to work. The generator itself was constructed with simplicity and economy as principal design criteria. The manufacturer of the generator, however, recognizing that users might require more precise electronic control, as in the present case, has developed a saturable reactor which can be used to regulate the output power precisely with a small control signal such as those which can be obtained from optical sensors. This reactor has been ordered, and it should be in operation within several weeks after the date of this report. In view of the difficulty in trying to grow crystals with the present system, no further attempts at crystal growth will be made until the new reactor control system is installed. In the view of the manufacturer of both the generator and the reactor, there should be no difficulty in maintaining a zone temperature as stable as required for this work.

III. SUMMARY AND DISCUSSION OF FUTURE PLANS

The results which have been obtained using polycrystalline thin films as microwave-frequency ultrasonic transducers are very encouraging. Even though the polycrystalline nature reduces the magnitude of the average magnetostriction from the single-crystal value, it is nevertheless possible to produce ultrasonic waves magnetostrictively with efficiency greater than that attainable with most other microwave-frequency transducer materials. Work is in progress to utilize single-crystal disks of pure gadolinium, terbium, dysprosium, holmium, and erbium as ultrasonic transducers. It is anticipated that the efficiency of conversion of electromagnetic energy to ultrasonic energy can be as high as 20 per cent with properly oriented single-crystal materials. If such efficiency can be achieved, a real breakthrough in this area will have been accomplished, since the efficiencies of other materials at high frequencies do not exceed one per cent. It is expected that results with single-crystal transducers will be obtained early in the second six-month phase of this program.

The results concerning ultrasonic wave propagation in single-crystal rare-earth materials are also quite interesting. Among other things, these results have revealed that there is indeed a very strong interaction between spin waves and elastic waves in

terbium, and that this material should be very useful as an ultrasonic transducer. Furthermore, the extremely sharp variation of ultrasonic attenuation with local magnetic field strength in certain temperature ranges leads to the possibility of the development of very useful ultrasonic modulators or switches which may find numerous applications in modern communications and signal processing systems.

Finally, although success has not yet been achieved in the attempt to grow single crystals of materials rich in the rare earths, the major obstacle seems to have been solved, and production of single crystals of the rare-earth elements, alloys, and intermetallic compounds needed for this program should commence very soon. In the interim period, arrangements are being made to secure small samples of alloys and intermetallic compounds (rare-earth-cobalt compounds, for example) which have been produced in other laboratories. When such materials become available to this research program, it will be possible to begin investigation of the dynamic magnetoelastic properties of materials which have both large magnetostriction and very high Curie temperatures. If these materials prove to be useful as transducers, then the need for operation at cryogenic temperatures, essential in the case of the pure rare earths, will no longer exist.

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